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The Effect of Cesium Vapour on the Bulk Conductivity of Plasma - Sprayed Spinel

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1. Introduction

The potential advantages of using magnesium aluminate spinel ($MgAl_2O_4$) in the thermionic fuel elements (TFEs) of nuclear heated space reactors have been described in a previous report <1>. In particular, its apparent resistance to radiation damage is attractive. In ref. <1> it was demonstrated that the surface electrical conductivity of single crystal spinel in cesium (Cs) vapour was of a similar magnitude, but in fact somewhat lower than that of sapphire. On this basis we concluded that, from the point of view of surface electrical degradation in Cs, single crystal spinel would be suitable for use as the insulator in the metal-ceramic seals in a TFE. The question then arises as to the possibility of using spinel, in plasma-sprayed form, as the collector insulator, instead of alumina (the material presently used). The potential benefits of spinel are, if anything, even greater here since the combined effects of radiation, temperature and high electric fields are most severe for this insulator. Under normal operating conditions this insulator is not exposed to Cs vapour. However if a metal-ceramic seal should leak then Cs can diffuse into the helium gap between the collector and the NaK coolant channel and coat the outside of the plasma-sprayed insulating layer. In a previous report <2> we have demonstrated that Cs vapour is able to penetrate the bulk of plasma-sprayed (ps) alumina and increase its electrical conductivity by many orders of magnitude. In this report we describe the results of a number of similar experiments performed on ps spinel. The experimental techniques have been described in ref. <2> and will not be repeated here.

2. Sample Preparation and Conductance Parameters

Sample preparation was carried out under the supervision of Dr. R. Neiser, SNL <3>. A layer of approximately 140µm of spinel was sprayed onto the surface of a 1" diameter, 1mm thick niobium disc. Metallographic cross sections were made of the samples and optical microscopy at 200x and 500x magnification revealed some porosity. The degree of porosity was qualitatively comparable to that of the alumina samples produced for the experiments described in ref. <2>. However no quantitative porosity measurements were made. Guarded niobium electrodes, around 500nm thick, were applied to the insulator surface. The bulk conductivity σ_b was computed from measured values of the bulk conductance G_b. The relationship between the two quantities for the guarded electrode configuration is

$$\sigma_b = G_b\left(\frac{t}{\pi(r_0-\delta)^2}\right) \quad . \tag{1}$$

In this equation t is the coating thickness and r_0 is the radius of the centre electrode plus D, where D is one half of the difference between the centre and guard electrode radii. δ is a correction factor which accounts for fringing fields. It is given by the following equation <4>

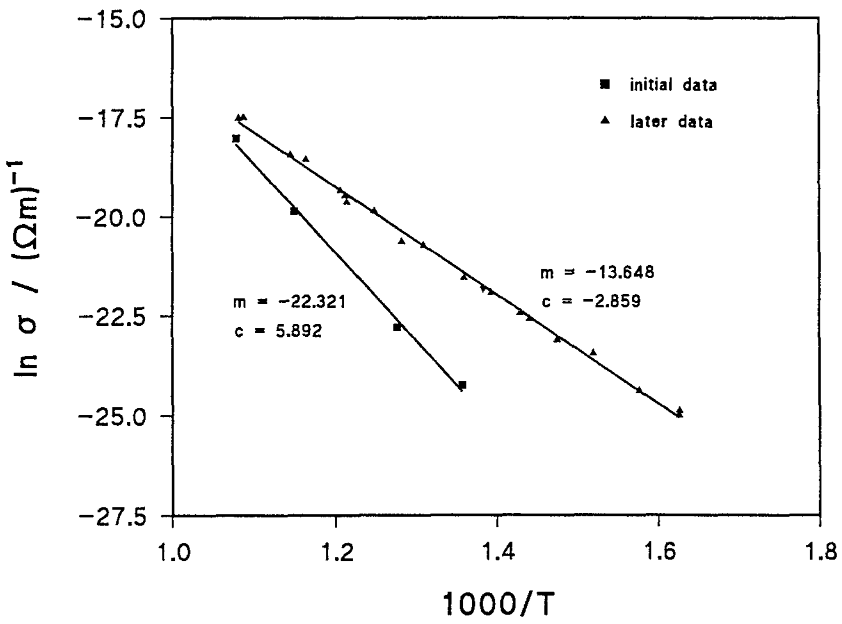
$$\delta = \frac{2t}{\pi} \ln\left\{ \cosh\left(\frac{\pi D}{2t} \right) \right\} \quad . \tag{2}$$

For our samples the values of these parameters are: t = 140 μm, r_0 = 6.0 mm, D = 1.5 mm. Using these values the numerical relationship between bulk conductivity and conductance is determined to be

$$\sigma_b = 2.143 G_b \quad (\Omega\ \mathrm{m})^{-1} \quad . \tag{3}$$

3. Initial Sample Characterization

Prior to exposure to Cs vapour the bulk electrical conductivity, σ_b, of the ps spinel was measured. There was significant variability in the sample conductance during the first two days over which measurements were made. This phenomenon had also been observed with the ps alumina <2> and was attributed to the gradual release of water vapour and other adsorbed gases from the internal pores of the material. The degree of variation was smaller with spinel than alumina. This is consistent with the fact that, in general, ps spinel is less hygroscopic than ps alumina <5>. Once the sample conductance had stabilized measurements were made as a function of sample temperature. These results are shown in fig. 1, together with some of the initial data, in order to indicate the magnitude of the changes which occur due to sample outgassing.



10^3 / T	T (K)	T (°C)
1.0	1000	727
1.1	909	636
1.2	833	560
1.3	769	496
1.4	714	441
1.5	667	394
1.6	625	352
1.7	588	315
1.8	556	283
2.0	500	227

Fig. 1. Bulk conductivity of ps spinel prior to Cs exposure.

The upper line (data indicated by triangles) shows the conductivity after sample outgassing. The data have an Arrhenius form, with an activation energy and pre-exponential factor of

$$E = (1.18 \pm 0.016)\ \text{eV}\ ,$$

$$\ln\sigma_0 = -2.859 \pm 0.24\ ;\quad \sigma_0 = 5.73 \times 10^{-2}\ (\Omega\ \text{m})^{-1}\ .$$

3. Effect of Exposure to Cs Vapour

Just as was found for ps alumina, the effect of Cs on σ_b for spinel is a rapid increase in its magnitude. In fig. 2 we compare the pre-exposure σ_b data with that obtained shortly after exposure to Cs at 0.1 Torr. The two data sets corresponding to Cs at 0.1 Torr were taken on two different days.

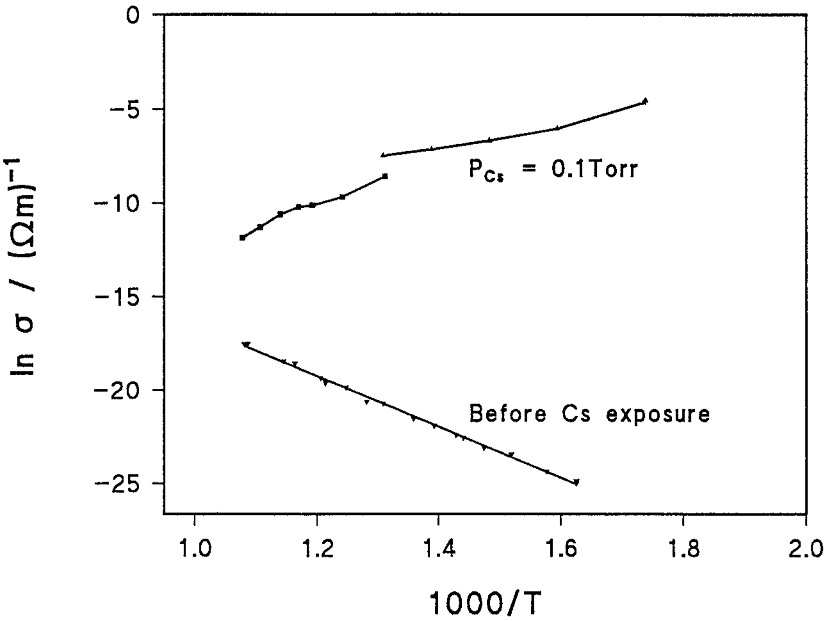


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Fig. 2. Effect of Cs on the bulk conductivity of ps spinel

At the lower temperatures σ_b has increased by about eight orders of magnitude. At higher temperatures, more relevant to TFE operations, the increase is two to three orders of magnitude. Together with the increase in the magnitude of σ_b , the trend in the temperature dependence has reversed. Increasing temperatures now lead to lower conductivity values. However the data are approximately 'Arrhenius' (i.e. straight line plot for ln σ_0 versus 1/T), but the sign of the exponent has changed.

4. Pressure Dependence

Measurements of σ_b were made as a function of Cs pressure over the range of approximately 0.1 to 0.9 Torr, at a constant sample temperature of 673 K. The range of Cs pressures in these experiments is not as large as that in the corresponding experiments with alumina <2>. However we do cover the range of pressures most relevant to TFE operation. The results are shown in fig. 3.

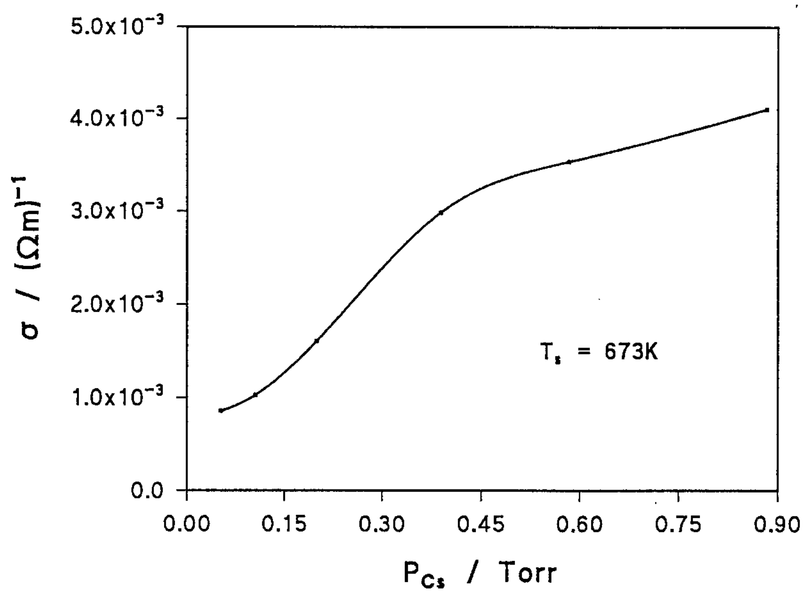
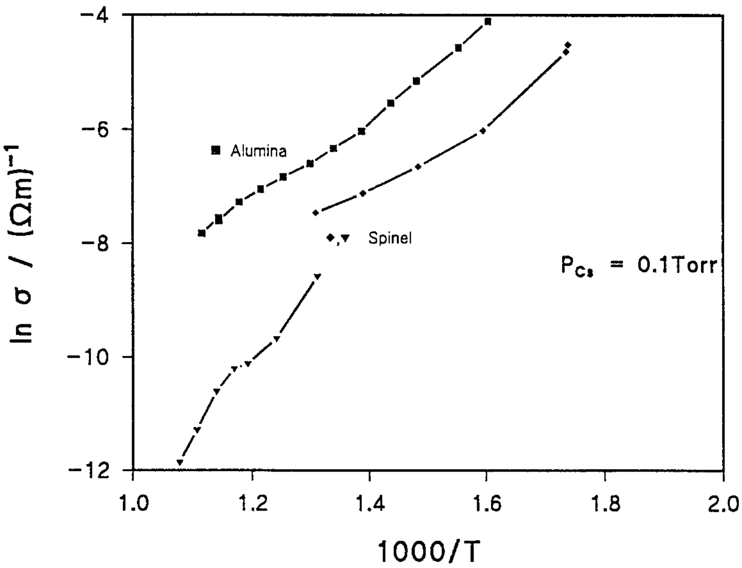


Fig. 3. Variation of σ_b with Cs pressure at a constant sample temperature of 673K

The trend for spinel is similar to that displayed by alumina. We note once more that this is in sharp contrast to the very weak pressure dependence observed for the surface conductivity of single crystal material <1>.

5. Comparison of Spinel With Alumina

In fig. 4 we present a comparison of the temperature variation of the bulk conductivity of spinel and alumina. The alumina data is taken from ref. <2>.



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1.7	588	315
1.8	556	283
2.0	500	227

Fig. 4. Temperature variation of the bulk conductivity of ps alumina and spinel exposed to Cs vapour at 0.1 Torr

The trend for conductivity to decrease with increasing temperature is similar for both materials. However the magnitude of the conductivity of the spinel sample is consistently smaller than that of the alumina sample. It is smaller by around one order of magnitude at the higher temperatures.

In fig. 5 we present a comparison of the pressure variation of the bulk conductivity of spinel and alumina, at a constant sample temperature of 673 K.

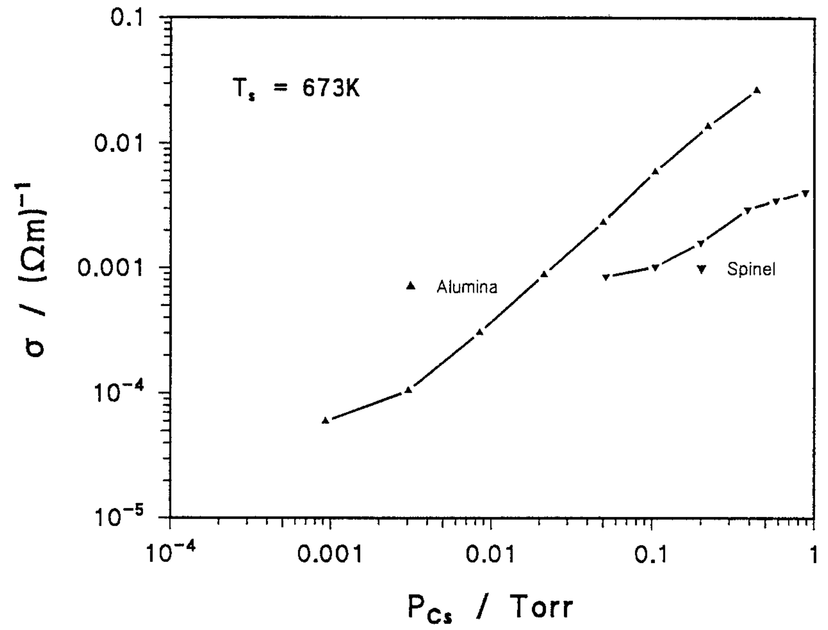

Fig. 5. Pressure variation of the bulk conductivity of ps alumina and spinel exposed to Cs vapour at 0.1 Torr

Again we see that the spinel sample consistently has a lower bulk conductivity than the alumina sample.

6. Discussion

Our results clearly indicate that, in the particular samples measured, spinel has a lower bulk electrical conductivity than alumina. There are three possibilities in interpreting this result:

(i) the spinel sample has a lower porosity than the alumina sample
(ii) ps spinel has an intrinsically lower conductivity than ps alumina in the presence of Cs
(iii) both of the above.

On the basis of our electrical measurements alone we are unable to discriminate between these three possibilities. However that is not to say that a discrimination could not be made with additional information. In fact independent porosity measurements (utilizing for example mercury intrusion porosimetry - MIPS) could determine the relative sample porosity. With regard to (ii) we can make the following two observations. Firstly we note that on a microscopic scale the ps materials consist of crystalline particles into which it should be just as difficult for

Cs to penetrate as for a macroscopic single crystal. Therefore what we have been describing as "bulk" conductivity is probably the result of conduction along internal surfaces in the plasma-sprayed material. Secondly, our results for the effect of Cs on the surface conductivity of single crystal alumina and spinel <1> show that spinel is lower, by about an order of magnitude. Taken together these two points suggest that (ii) may be true.

7. Summary

We have presented data for both the temperature and pressure variations of the effect of Cs on the bulk conductivity of ps spinel. We have demonstrated that, under exposure to Cs vapour, our plasma-sprayed spinel samples have a lower bulk electrical conductivity than the ps alumina tested in ref <2>. The implication of our results for TFE technology should be regarded as follows. The degree of improvement in the behaviour of spinel over alumina in a Cs environment, taken in isolation, is not sufficient to warrant a recommendation to use spinel henceforth in future TFEs. However, if further evidence should come to light regarding the unsuitability of alumina (for example, due to some radiation induced electrical degradation phenomena) then spinel may be regarded as a suitable replacement candidate and no new concerns need arise over its behaviour in a Cs environment.

Acknowledgments

We would like to thank Mr. J. Watson for his assistance in constructing the experimental facility and his help in performing these experiments.

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<4> W.G. Amey and F. Hamburger, Proc. Amer. Soc. Test Materials 49 , 1079 (1949).

<5> R.A. Neiser, private communication.